tended to sublime at high vacuum, had m.p. 89–90° (lit. m.p. 89°,[40] 86.5–87.5°[41]); λ_{max} 258 mμ (ϵ 315 sh), 264 (390), 271 (350); λ_{min} 241 mμ (ϵ 155); 269 (280).

Anal. Calcd. for $C_{10}H_{11}NO$ (161.21): C, 74.51; H, 6.88. Found: C, 74.32; H, 7.04.

Preparation of 2-Naphthylamine (IX) Hydrochloride from 2-Tetralone Oxime (VIII).—A solution of 0.20 g. of 2-tetralone oxime (VIII) in 8.0 ml. of saturated methanolic hydrogen chloride was refluxed for 1 hr. and then stripped to dryness at reduced pressure. The white solid residue was dissolved in dilute hydrochloric acid (2.0 ml. of concentrated hydrochloric acid diluted to 20 ml. with water), filtered, and made basic. The white solid separated, was collected, washed with water, dissolved in 4 ml. of methylene chloride, dried briefly over anhydrous sodium sulfate, and filtered. The solution was saturated with gaseous hydrogen chloride and chilled to 0°, giving 0.13 g. (58%) of white solid IX hydrochloride, m.p. 241–242.5°; λ_{max} 236 mμ (ϵ 53,420), 268 (4900 sh), 279 (5900), 290 (4270 sh), 338–340 (1260); λ_{min} 257 mμ (ϵ 3540), 305 (470) (the ultraviolet absorption spectrum is the same as that reported previously[42] for IX).

Anal. Calcd. for $C_{10}H_{10}NCl$ (179.65): C, 66.86; H, 5.61; N, 7.80; Cl, 19.73. Found: C, 66.87; H, 5.75; N, 7.69; Cl, 20.00.

Reduction of 2-Amino-1-indanone (V) Hydrochloride with 5% Palladium-on-Charcoal Catalyst.—A mixture of 1.50 g. of V-hydrochloride and 0.75 g. of 5% palladium on charcoal in 23 ml. of glacial acetic acid and 1.2 ml. of concentrated sulfuric acid was shaken in a hydrogen atmosphere at room temperature and 45 p.s.i.g. of pressure. The reaction mixture was worked up as described to give 0.97 g. (69.8%) of III hydrochloride, m.p. 234–238°, slightly contaminated according to paper chromatography.

Acknowledgment.—We are grateful to Mr. B. Korzun, Mr. S. Brody, and Mr. P. Keegan for the paper chromatographic work. The microanalytical data were kindly supplied by Mr. L. Dorfman and his associates of the Ciba Technical Services Section. We thank Dr. G. Papariello and Miss A. Finan for the molecular weight determination by X-ray diffraction, Mr. L. Dorfman for valuable discussions, and Mr. M. Linfield for technical assistance.

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[40] J. v. Braun, O. Braunsdorf, and G. Kirschbaum, *Ber.*, **55**, 3648 (1922).

[41] F. Straus and A. Rohrbacher, *ibid.*, **54**, 40 (1921).

[42] E. A. Steck and G. W. Ewing, *J. Am. Chem. Soc.*, **70**, 3397 (1948); R. N. Jones, *ibid.*, **67**, 2127 (1945).

The Synthesis of 3-Ethyl-4-methylphenol and 3-Isopropyl-4-methylphenol from 3,4-Dimethylphenol *via* Trichloromethyl Intermediates[1]

MELVIN S. NEWMAN AND FRIEDRICH BAYERLEIN

Evans Chemistry Laboratory of The Ohio State University, Columbus 10, Ohio

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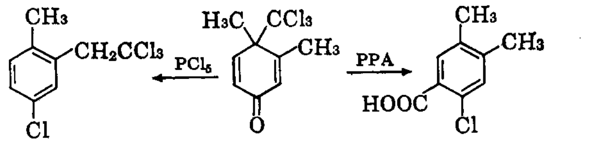
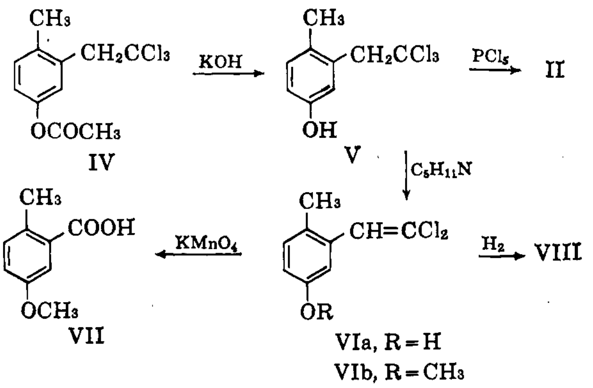
On refluxing solutions of 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone (I) in acetic anhydride containing an acid, rearrangement to the acetate of 4-methyl-3-(β,β,β-trichlorethyl)phenol (V) occurs in high yield. Treatment of V with piperidine yields 4-methyl-3-(β,β-dichlorovinyl)phenol (VIa) which on hydrogenation is converted into 3-ethyl-4-methylphenol (VIII). Condensation of VIII with carbon tetrachloride (aluminum chloride) affords 3-ethyl-4-methyl-4-trichloromethyl-2,5-cyclohexadienone (IX) which may be converted into 4-methyl-3-isopropylphenol (XIII) by a series of reactions analogous to those by which V is converted into VIII.

The rearrangements of 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone (I) to 4-methyl-3-(β,β,β-trichloroethyl)chlorobenzene (II) on treatment with phosphorus pentachloride and to 2-chloro-4,5-dimethylbenzoic acid (III) on treatment with polyphosphoric acid (PPA) have been described.[2] In these types of reaction the nuclear oxygen is replaced by chlorine. We now describe acid-catalyzed rearrangements of I, and of the corresponding 3-ethyl analog IX, in which the nuclear oxygen is retained. By means of these reactions and further reactions described later, the syntheses of 3-ethyl-4-methylphenol (VIII) from 3,4-dimethylphenol and of 3-isopropyl-4-methylphenol (XIII) from VIII have been accomplished.



II I III

When solutions of I in acetic anhydride containing small amounts of concentrated sulfuric acid (or of hydrogen chloride) were refluxed for from three to seven hours, yields of over 90% of 4-methyl-3-(β,β,β-trichloroethyl)phenyl acetate (IV) were obtained. The structure of IV was established by the following method: Brief alkaline hydrolysis of IV yielded 4-methyl-3-(β,β,β-trichloroethyl)phenol (V) which on heating with piperidine afforded 4-methyl-3-(β,β-dichlorovinyl)phenol (VIa). Methylation of VIa yielded VIb which on oxidation yielded 5-methoxy-2-methylbenzoic acid (VII) identical with VII prepared by another route.[3] All yields were high. In addition, treatment of V with phosphorus pentachloride yielded a small amount of II.[2] Identity of the two samples of II was demonstrated by comparison of the infrared spectra.



IV V VII VIa, R = H VIb, R = CH3

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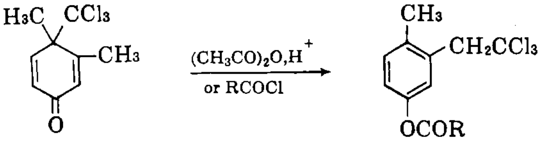
[1] This research was supported by the United States Air Force under contract no. AF49(638)-277 monitored by the Air Force Office of Scientific Research of The Air Research and Development Command.

[2] M. S. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 6450 (1959).

[3] Dr. D. Pawellek prepared VII by methylation of 5-hydroxy-2-methylbenzoic acid (see ref. 8, this paper) in aqueous sodium hydroxide using dimethyl sulfate.

When the dienone I was heated with aroyl chlorides, acyl derivatives IVa, corresponding to IV, were formed in high yield. However, when 4-methyl-4-trichloromethyl-2,5-cyclohexadienone was treated similarly with acetic anhydride–sulfuric mixtures or with acyl chlorides, the dienone was recovered in high yield.

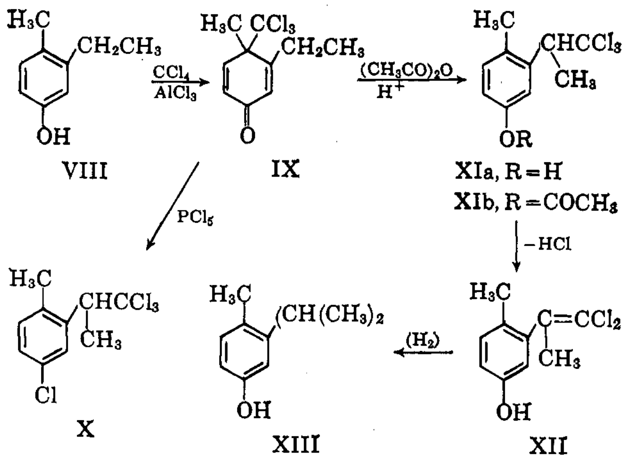


I

IVa, R = aryl

On catalytic hydrogenation over platinum, VIa was reduced in high yield to 3-ethyl-4-methylphenol (VIII). Attempts to reduce V under similar conditions failed as there was no uptake of hydrogen.

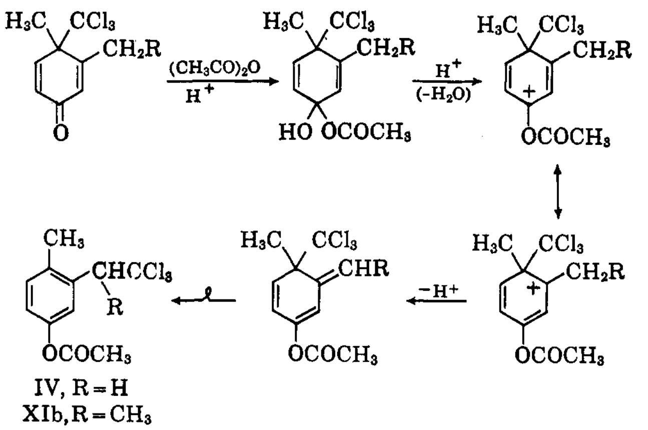
Condensation of VIII with carbon tetrachloride using aluminum chloride produced 3-ethyl-4-methyl-4-trichloromethyl-2,5-hexadienone (IX). As in comparable experiments starting from I, IX was converted with phosphorus pentachloride into 4-methyl-3-(β,β,β-trichloroisopropyl)chlorobenzene (X), and with acetic anhydride containing acid into 4-methyl-3-(β,β,β-trichloroisopropyl)phenyl acetate (XIb), although the yields were less than in the case of I.



Treatment of XIa with basic reagents afforded 4-methyl-3-(α-methyl-β,β-dichlorovinyl)phenol (XII) and catalytic reduction of XII yielded 3-isopropyl-4-methylphenol (XIII). Thus, the reactions of IX parallel those of 3,4-dimethyl-4-trichloromethyl-2,5-cyclohexadienone (I).

The rearrangements of I to IV and of IX to XIb probably proceed by a mechanism similar to that proposed for the rearrangement of I to II,[4] as shown (col. 2).

In conclusion, it is noteworthy that in all dienone–phenol rearrangements we and others have studied in which a trichloromethyl group migrates[2,4,5] a 1:3- or 1:5-shift occurs and the migration may be pictured as taking place in a neutral molecule.



Experimental[6]

3,4-Dimethyl-4-trichloromethyl-2,5-cyclohexadienone (I) was prepared essentially as described[2] except that the crude mixture of reaction products after isolation in the usual way[6] was vacuum distilled in order to avoid the time-consuming steam distillation.[2] The fraction boiling near 135° (1 mm.) was crystallized from petroleum ether (b.p. 65–70°) to yield I as colorless needles, m.p. 60–61°, in 61–70% yields.

4-Methyl-3-(β,β,β-trichloroethyl)phenol (V) and Esters Thereof (IV).—In the best of several runs a solution of 200 g. of I in 1200 ml. of acetic anhydride containing 4 ml. of concentrated sulfuric acid was held at reflux for 5 hr. After removal of most of the acetic anhydride under reduced pressure, crude IVa (R = CH_3), 230 g. (98%) was obtained by distillation (without removal of sulfuric acid) as an oil, b.p. 134–136° (11 mm.), which soon crystallized. Crystallization from petroleum ether yielded the analytical sample, m.p. 76.0–77.0°, with little loss.

Anal. Calcd. for $C_{11}H_{11}Cl_3O_2$: C, 46.9; H, 3.9; Cl, 37.8. Found: C, 46.8; H, 3.8; Cl, 37.7.

Yields in the 80–95% range were obtained under a variety of conditions in which the amount of acid, acetic anhydride, and time of heating were varied. In two runs anhydrous hydrogen chloride was passed in slowly during the reflux period instead of sulfuric acid. In two runs 5.0 g. of I and 25 ml. of acetyl chloride were held at reflux for 10 and 15 hr. IVa was obtained in 88 and 93% yields, respectively. Under similar conditions 4-methyl-4-trichloromethyl-2,5-cyclohexadienone was recovered unchanged.

Hydrolysis of the acetate IVa (R = CH_3) in aqueous methanol containing about two equivalents of potassium hydroxide by heating to reflux for several minutes yielded after acidification 4-methyl-3-(β,β,β-trichloroethyl)phenol (V) as colorless prisms in almost quantitative yield. The analytical sample, obtained by crystallization from petroleum ether, melted at 111.0–112.0°.

Anal. Calcd. for $C_9H_9Cl_3O$: C, 45.1; H, 3.8; Cl, 44.4. Found: C, 45.3; H, 3.9; Cl, 44.2.

When a mixture of 5.0 g. of I in 50 ml. of benzoyl chloride was held at 140° for 8 hr., and then distilled, 6.7 g. (93%) of IVa (R = C_6H_5) was obtained. Recrystallization from ethanol yielded the analytical sample, m.p. 118.0–119.0°.

Anal. Calcd. for $C_{16}H_{13}Cl_3O_2$: C, 55.9; H, 3.8; Cl, 31.0. Found: C, 55.9; H, 3.9; Cl, 30.9.

When solutions of 5.0 g. of I in 40 ml. of xylene containing 40 g. of *p*-nitrobenzoyl chloride, *p*-methoxybenzoyl chloride, and mesitoyl chloride, respectively, were heated at reflux for 10 hr., the corresponding esters, IVa (R = *p*-$C_6H_4NO_2$), m.p. 157–158°; IVa (R = *p*-$CH_3OC_6H_4$), m.p. 99–100°; and IVa [R = 2,4,6-$(CH_3)_3C_6H_2$], m.p. 116–117°, all recrystallized from ethanol, were obtained in 85, 70, and 60% yields after isolation in the usual way.[6]

Anal. Calcd. for $C_{16}H_{12}Cl_3NO_4$: C, 49.4; H, 3.1; Cl, 27.4; N, 3.6. Found: C, 49.4; H, 2.9; Cl, 27.1; N, 3.8. Calcd. for $C_{17}H_{15}Cl_3O_3$: C, 54.6; H, 4.0; Cl, 28.5. Found: C, 54.9; H,

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[4] M. S. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 4300 (1959).

[5] K. Auwers and W. Julicher, *Ber.*, **55**, 2167 (1922); R. L. Tse and M. S. Newman, *J. Org. Chem.*, **21**, 638 (1956); M. S. Newman, J. Eberwein, and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 6454 (1959); and M. S. Newman, D. Pawellek, and S. Ramachandran, *ibid.*, **84**, 995 (1962).

[6] The term "worked up in the usual way" means that an ether–benzene (about 1:1) solution of the reaction products was washed with dilute acid, and/or alkali, and a saturated solution of sodium chloride. This solution was then filtered through anhydrous magnesium sulfate and the solvents removed by distillation. The residue was either distilled or crystallized as indicated by properties of products. Analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn., by the Schwarzkopf Laboratory, Woodside, N. Y., and Spang Microanalytical Laboratory, Ann Arbor, Mich.

4.1; Cl, 28.5. Calcd. for $C_{19}H_{19}Cl_3O_2$: C, 59.2; H, 5.0; Cl, 27.6. Found: C, 59.4; H, 5.2; Cl, 27.4.

Each of these esters, except the mesitoate, yielded V on hydrolysis.

3-(β,β-Dichlorovinyl)-4-methylphenol (VIa).—On heating a solution of V in excess (about 2.5–3 ml. per g.) piperidine at 75° for 10 hr., VIa was obtained in over 90% yield by pouring the reaction mixture into excess dilute hydrochloric acid. The product was purified by distillation, b.p. 110° (1 min.), and by crystallization from petroleum ether. The analytical sample melted at 89–90°.

Anal. Calcd. for $C_9H_8Cl_2O$: C, 53.3; H, 3.9; Cl, 34.9. Found: C, 53.3; H, 3.9; Cl, 34.9.

3-(β,β-Dichlorovinyl)-4-methylanisole (VIb).—A solution of 10.1 g. of VIa in 50 ml. of 2 *N* sodium hydroxide was treated with 7 g. of dimethyl sulfate for 3 hr. Then 50 ml. of concentrated ammonia was added and stirring continued for 30 min. Distillation of the neutral fraction isolated as usual yielded 9.1 g. (84%) of VIb, b.p. 94–95° (1 mm.).

Anal. Calcd. for $C_{10}H_{10}Cl_2O$: C, 55.4; H, 4.6; Cl, 32.7. Found: C, 55.4; H, 4.5; Cl, 32.6.

When a stirred solution of 2.2 g. of VIb in 25 ml. of pyridine was treated during 15 min., with a solution of 3.2 g. of potassium permanganate in 25 ml. of water and 15 ml. of pyridine, there was obtained from the acid fraction of the products 1.5 g. (90%) of 5-methoxy-2-methylbenzoic acid, m.p. 145–146°. The mixture melting point with an authentic sample[3] of acid was not depressed.

3-Ethyl-4-methylphenol (VIII).—A solution of 5.0 g. of VIa in 100 ml. of methanol was reduced over 0.5 g. of platinic oxide catalyst with a hydrogen pressure of 40–50 p.s.i. In general reductions proceeded smoothly to yield about 3.0 g. (90%) of VIII, b.p. 100–101° (4 mm.). Crystallization from petroleum ether, (b.p. *ca.* 40°) yielded colorless fine needles of VIII, m.p. 35–36°.

Anal. Calcd. for $C_9H_{12}O$: C, 79.4; H, 8.9. Found: C, 79.3; H, 9.0.

The *p*-nitrobenzoate crystallized as plates, m.p. 117–118°, from ethanol.

Anal. Calcd. for $C_{16}H_{15}NO_4$: C, 67.4; H, 5.3; N, 4.9. Found: C, 67.6; H, 5.4; N, 5.1.

3-Ethyl-4-methyl-4-trichloromethyl-2,5-cyclohexadienone (IX).—A solution of 60.00 g. of VIII in 300 ml. of carbon disulfide was added during 1 hr. to a stirred slurry of 96 g. of aluminum chloride in 300 ml. of carbon disulfide containing 93 g. of carbon tetrachloride at room temperature. The stirred mixture was heated to reflux for 1 hr. and was then poured on ice. The organic layer was separated and treated as usual. Distillation afforded 63 g. (57%) of an oil, b.p. 129–132° (2 mm.) Crystallization from petroleum ether, b.p. 40°, yielded the analytical sample of IX, m.p. 35–36°. In further work on IX, the once-distilled oil was used.

Anal. Calcd. for $C_{10}H_{11}Cl_3O$: C, 47.4; H, 4.4; Cl, 42.0. Found: C, 47.5; H, 4.4; Cl, 41.8.

The product IX has a pleasant camphoraceous odor and forms a red 2,4-dinitrophenylhydrazone, m.p. 181–182° dec.

Anal. Calcd. for $C_{16}H_{15}Cl_3N_4O_4$: C, 44.3; H, 3.5; N, 12.9; Cl, 24.5. Found: C, 44.3; H, 3.6; N, 12.9; Cl, 24.4.

4-Methyl-3-(β,β,β-trichloroisopropyl)chlorobenzene (X).—To 5.1 g. of IX was added 4.2 g. of phosphorus pentachloride. The mixture, after standing 12 hr. at room temperature, was heated for 1 hr. at 140°. Distillation afforded 2.7 g. (55%) of X as a colorless oil, b.p. 100–120° (bath temperature) (2 mm.). Redistillation yielded the analytical sample.

Anal. Calcd. for $C_{10}H_{10}Cl_4$: C, 44.2; H, 3.7; Cl, 52.1. Found: C, 44.0; H, 3.6; Cl, 52.4.

No further work was done with X. The structure is assumed by analogy as the structure of the rearrangement product of IX in acetic anhydride has been proved (see succeeding paragraph).

4-Methyl-3-(β,β,β-trichloroisopropyl)phenyl Acetate (XIb).—A solution of 10.0 g. of IX in 100 ml. of acetic anhydride was refluxed for 24 hr. with dry hydrogen chloride being passed in continuously. Most of the acetic anhydride was removed under vacuum and the acetate XIb isolated in 75% yield after the usual treatment[6] as an oil [bath temperature 160–170° (1 mm.)] which soon crystallized. Recrystallization from ethanol yielded colorless prisms, m.p. 72–73°.

Anal. Calcd. for $C_{12}H_{13}Cl_3O_2$: C, 48.8; H, 4.4; Cl, 36.0. Found: C, 48.9; H, 4.6; Cl, 35.8.

4-Methyl-3-(β,β,β-trichloroisopropyl)phenol (XIa).—A solution of 5.0 g. of VIb in 50 ml. of methanol containing a slight excess of 10% potassium hydroxide was heated for 10 min. After acidification the phenol XIa was isolated as a colorless solid in 89% yield. Recrystallization from petroleum ether yielded fine needles, m.p. 87–88°. The *p*-nitrobenzoate, recrystallized from ethanol, melted at 129–130°.

Anal. Calcd. for $C_{10}H_{11}Cl_3O$: C, 47.4; H, 4.3; Cl, 42.0. Found: C, 47.5; H, 4.2; Cl, 41.9.

4-Methyl-3-(α-methyl-β,β-dichlorovinyl)phenol (XII).—A mixture of 5.65 g. of XIa and 10 ml. of piperidine was heated at reflux for 4 hr. After working up in the usual way, XII was obtained as a colorless oil, b.p. 123–125° (1.2 mm.), in 81% yield. When these reagents were heated in refluxing benzene no reaction occurred. As great difficulty in securing a pure sample for analysis was experienced, this product was characterized as the *p*-nitrobenzoate, m.p. 98–99°.

Anal. Calcd. for $C_{17}H_{13}Cl_2NO_4$: C, 55.8; H, 3.6; Cl, 19.4; N, 3.8. Found: C, 55.8; H, 3.8; Cl, 19.7; N, 4.0.

3-Isopropyl-4-methylphenol (XIII).—Catalytic reduction of XII in ethanol over platinum (40 p.s.i. of hydrogen) went smoothly to yield XIII, b.p. 89–90° (0.5–1 mm.). It was possible to crystallize XIII in the form of fine needles, m.p. 38–39°, but comparison with known XIII was best effected through the *p*-nitrobenzoate, m.p. and m.m.p. 108–109°.

Anal. Calcd. for $C_{10}H_{14}O$: C, 80.0; H, 9.4. Found: C, 80.1, 80.0; H, 9.3, 9.5. Calcd. for $C_{17}H_{17}NO_4$: C, 68.2; H, 5.7. Found: C, 68.2; H, 5.8.

An authentic sample of XIII was prepared by the following reactions.

5-Hydroxy-2-methylbenzoic Acid.[7]—In a 1-l. steel bomb was placed 100 g. of dipotassium 2-naphthol-6,8-disulfonic acid and 400 g. of 50% sodium hydroxide containing 0.5 g. of iron rust.[8] The bomb was held at 275–280° for 17 hr. After cooling, the pH of the dark brown solution was adjusted to 7.5 by addition of hydrochloric acid, and then charcoal (Darco G-60) was added. Acidification of the filtrate yielded 26.8 g. (67%) of acid which was recrystallized from water to yield the desired acid, m.p. 179–181°, in 54% over-all yield.

4-Methyl-3-(α-hydroxy-α-methylethyl)phenol.[7]—The methyl ester, m.p. 76–77.5°, prepared in 90% yield,[9] in tetrahydrofuran was added to excess ethereal methylmagnesium bromide. Distillation of the product isolated in the usual way yielded the tertiary alcohol, b.p. 100–104° (5 mm.), in 60% yield. The analytical sample, obtained by crystallization from benzene, melted at 139–140°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.3; H, 8.5. Found: C, 72.0; H, 8.3.

Catalytic hydrogenation of the diol in ethanol over a palladium-on-carbon catalyst afforded 3-isopropyl-4-methylphenol (XIII) in high yield.

5-Methoxy-2-methylbenzoic Acid (VII).—A stirred solution of 76 g. of 5-hydroxy-2-methylbenzoic acid in 1 l. of water containing 80 g. of sodium hydroxide was treated with 126 g. of dimethyl sulfate. After 3 hr. the solution was heated to reflux for 20 min. and worked up in the usual way. A 95% yield of crude product was obtained. A recrystallized sample of VII[10] melted at 151.0–151.5°.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.0; H, 6.1. Found: C, 65.1; H, 6.0.

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(7) These experiments were performed by Dr. E. A. Grannen, Jr.

(8) Th. Zincke and H. Fischer, *Ann.*, **350**, 247 (1906). A larger quantity of this acid was made available to us by the Upjohn Co., Kalamazoo, Mich., to whom we express our thanks.

(9) R. O. Clinton and S. C. Laskowski, *J. Am. Chem. Soc.*, **70**, 3135 (1948).

(10) O. Jacobsen, *Ber.*, **16**, 1962 (1883), gives a m.p. of 146° but no analytical data.